The effect of preparation method on pigmentary properties of manganese doped cassiterite pigments

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Abstract

The presented work deals with the possibility of synthesis of blue-violet cassiterite pigments in which a part of tin ions was substituted by cobalt and manganese ions. In this case, phosphorous ions are used as charge-compensating elements. The compounds of formula $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ were prepared by solid state reaction using the classical ceramic method and also by the method of mechanical activation. The goal was to develop conditions for synthesis and the most suitable preparation method of these pigments. The temperature range was chosen from 1350 to 1500 °C. The synthesised pigments were characterised in terms of colour properties after their application into the transparent ceramic glaze P 074 91 and into the organic binder. They were also studied with respect to their phase composition as well as the particle size distribution.

Keywords: pigments, colour, solid state reaction, tin dioxide, cassiterite

Introduction

Currently, there is a significant increase in demand for colour inorganic pigments [1]. These materials can be used for colouring ceramic glazes, porcelain enamels, plastics, inks, external paints, building materials, foods, etc. As known, inorganic pigments are composed of metal oxides, mixed oxides, sulphides, phosphates, carbonates [2]. Cassiterite pigments are based on tin dioxide respectively they are mixed oxides, where tin dioxide is the main component. These pigments belong to the group of ceramic pigments with high thermal and chemical stability and they are based on tetragonal mineral cassiterite SnO_2 (a = 0.4737 nm and c = 0.3185 nm) [3]. Their crystal structure is modified by doping elements (chromophores), which can change the cell parameters. The structure of the host lattice is preserved, but it can be disordered [4].

In this research, the ions of cobalt and manganese as chromophores were chosen. All blue ceramic pigments known currently (except the vanadium-zirconium blue, CPMA 14-42-2) are based on doping of thermally stable crystal lattice by ions of cobalt [5, 6]. However, the colour performance of cobalt pigment depends on their thermal stability, chemical reactivity towards the glaze components, as well as on the coordination of Co^{2+} ions (tetrahedral coordination is preferred to octahedral) [7]. Due to Co ions (II) have oxidation state lower than (IV), the second element with oxidation state higher than (IV) is always added in order to fulfil the electroneutrality of the structure. In this case, P (V) ions are used as charge-compensating elements.

In this presented work, the synthesis of manganese-doped cassiterite pigments is studied. First, the compounds of formula $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ were prepared by the classical ceramic method. This method involves homogenisation of

the mixture of the corresponding compounds and their subsequent calcination at high temperatures. The compound of the same formula was also prepared by dry mechanical activation.

Experimental

Pigments $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ were synthesised by two methods of preparation. The both methods of the synthesis were based on the classical ceramic route, i.e. solid state reaction. The starting materials used for preparation of $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ pigments were SnO_2 (>99.9%, Alfa Aesar, Germany), $Co(OH)_2$ (99%, Shepherd Color Company, USA), $NH_4H_2PO_4$ (99.5%, Lachema a.s., Czech Republic) and MnO_2 (>99.9%, Lachema a.s., Czech Republic) weighed in suitable molar proportion and subsequently ground manually in a porcelain mortar to obtain a homogenous reaction mixture. The mixtures were calcinated in corundum crucibles in an electric resistance furnace. The heating of furnace was programmed with increasing temperature at a rate 10 °C.min^{-1} and the calcination temperature of 1350 - 1500 °C was maintained for three hours. All samples were gradually cooled to room temperature and ground in an agate mortar. The other method of solid state reaction (MA) was innovated by the mechano-chemical activation prior to calcination. The high energy milling process was carried out in a planetary mill Pulverisette 5 (Fritsch, GmbH Idar-Oberstein, Germany). The reaction mixtures were ground with agate balls (Ø10 mm) in a ball-to-powder weight ratio of 18:1. The milling was carried out for 5 hours at a rotational velocity of 200 rpm. The activated reaction mixtures were transferred into corundum crucibles and exposed to the same calcining process as in the previous method.

The calcinated powder samples were applied into an organic matrix (dispersive acrylic paint Parketol, Balakom a.s., Czech Republic) in mass tone and into medium temperature ceramic glaze P 074 91 (Glazura, s.r.o., Czech Republic), with the amount of a pigment sample 10 wt%. The glaze is characterised by the thermal expansion coefficient α = 56.8 .10^{-7} K^{-1}.For testing in the organic binder, the suspension containing 1 g of the sample and 1.5 cm^3 of binder was homogenized. This suspension was converted by a pestle to dense paste able to flowing. Coloured coating films were prepared by application of the paste on white nonabsorbing glossy paper. The coating layer of film was created by dragging the Bird´s applicator. Prepared coating films were kept to dry spontaneously in the open air. Then they were ready for an evaluation of colour properties of pigments into organic binder in mass tone. In the case of application into the ceramic glaze, an aqueous suspension containing 10 wt% of pigment and 90 wt% of transparent ceramic glaze with an appropriate amount of distilled water was prepared by hand-grinding. The suspension was applied by using the brush on unglazed ceramic tile and after drying in the air was glazed at 1050 °C for 15 min.

The crystal structures of the powdered materials were studied by X-ray diffraction analysis. The phase composition was determined using diffractometer D8 Advance (Bruker AXS, UK) equipped with a vertical goniometer of 17 cm in the 2Θ

range of 10-80°. X–ray tube with Cu anode (U = 40 kV, I = 30 mA), secondary graphite monochromator, scintillation NaI(Tl) counter, and X-ray of copper were used. Wavelength of the applied X-ray is Kα_1 = 0.15418 nm for angle 2Θ < 35° and Kα_2 = 0.15405 nm for angle 2Θ > 35°.

The colour properties of all final applications were objectively evaluated by measuring of spectral reflectance in the visible region of light (400-700 nm) by using a spectrophotometer ColorQuest XE (HunterLab, USA). Standard illuminant D65 was used as internationally recommended white daylight, measurement conditions were as follows: 10° supplementary standard observer, measuring geometry d/8°. The colour properties are described in terms of *CIE L*a*b** system (1976). The value *a** (the red-green axis) and *b** (the yellow-blue axis) indicate the colour hue. The value *L** represents the lightness or darkness of the colour as related to the natural grey scale. In the *L*a*b** system, it is described by numbers from 0 (black) to 100 (white). The value *C* (Chroma) represents saturation of the colour and determines colour purity. The colour hue of pigments is also possible to express as a hue angle *H°*. Hue angle *H°* is defined as starting at the +*a** axis and indicates the position of the sample in a*, b* diagram. It is expressed in degrees; *H°* = 350-35° (for red), *H°* = 35-70° (for orange), *H°* = 70-105° (for yellow), *H°* = 105-195° (for green), *H°* = 195-285° (for blue), *H°* = 285-350° (for violet). Chroma *C* and hue angle *H°* of samples were calculated according to the Eqs. (1) and (2).

$$C = (a^{*\,2} + b^{*\,2})^{\frac{1}{2}} \tag{1}$$

$$H° = \text{arctg}\ (b^*/a^*) \tag{2}$$

The total colour difference Δ*E*$_{CIE}$* in the CIE *L*a*b** diagram, which indicates the degree of colour difference between the two samples, is defined by the following equation (3), where Δ*L**, Δ*a**, Δ*b** are differences in *L**, *a** and *b** values between colour sample and colour of standard [8].

$$\Delta E_{CIE}{}^* = [(\Delta L^*)^2 + (\Delta a^*)^2\ (\Delta b^*)^2]^{\frac{1}{2}} \tag{3}$$

The crystal structures of the powdered materials were studied by X-ray diffraction analysis. The phase composition was determined using diffractometer D8 Advance (Bruker AXS, UK) equipped with a vertical goniometer of 17 cm in 2Θ range of 10-80°. X–ray tube with Cu anode (U = 40 kV, I = 30 mA), secondary graphite monochromator, scintillation NaI(Tl) counter, and X-ray of copper were used. The wavelength of the applied X-ray is Kα_1 = 0.15418 nm for angle 2Θ < 35° and Kα_2 = 0.15405 nm for angle 2Θ > 35°.

The particle size distribution of the synthesised pigments was measured using an equipment Mastersizer 2000/MU (Malvern Instruments, Ltd., UK). This device provides volumetric distribution and uses the laser diffraction on particles dispersed in a liquid medium. The particle size distribution was analysed by two lasers – red light (He–Ne laser with wavelength 633 nm) and blue light (laser diode with

wavelength 466 nm). The pigments were ultrasonically homogenized in solution of $Na_4P_2O_7$ (c = 0.15 mol dm^{-3}) for 120 s. The signal was evaluated on the basis of Fraunhofer diffraction. The measurement is performed in three steps, results are automatically calculated as average and presented as d_{10}, d_{50}, d_{90} and *span* values.

$$span = (d_{90} - d_{10})/d_{50} \tag{4}$$

Results and discussion

XRD analysis

The prepared powder compounds were studied by means of XRD analysis. The samples, which were prepared by the classical ceramic method, were single-phased at all synthesis temperatures. The only major crystalline phase corresponding with tetragonal cassiterite structure of SnO_2 (JCPDS No. 77-0452) with $P4_2/mnm$ symmetry was identified. The intensities of peaks increased with calcination temperature, which means that the peaks are the sharpest and the most intense at 1500 °C. The contraction of lattice constants confirmed the incorporation of Co (II) and Mn (IV) ions in SnO_2 host lattice (lattice parameters of pure SnO_2: a = 0.473700 nm and c = 0.318500 nm). The phase composition was also evaluated at pigments, which were prepared by dry mechanical activation. From the presented results it follows, that second minor phase corresponding to cubic SnP_2O_7 (JCPDS No. 29-1352) with Pa-3 symmetry was observed in the temperature range from 1350 to 1450 °C. The intensities of peaks increase with calcination temperature as in the case of pigments prepared by the classical ceramic method.

Tab. 1 The effect of preparation method and calcination temperature on the phase composition of powder $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$

Method of preparation	Temperature [°C]	Structure	a [nm]	c [nm]
Classical ceramic method	1350	tetragonal SnO$_2$	0.473700	0.318500
	1400		0.473700	0.318500
	1450		0.473700	0.318500
	1500		0.473738	0.318634
Dry mechanical activation	1350	tetragonal SnO$_2$	0.473700	0.318500
	1400	tetragonal SnO$_2$	0.473724	0.318660
		cubic SnP$_2$O$_7$	0.795839	-
	1450	tetragonal SnO$_2$	0.473700	0.318648
	1500	tetragonal SnO$_2$	0.473700	0.318668

The colour properties

The goal was to develop conditions for the synthesis of cassiterite pigments and determine the influence of preparation method on the colouring effects of these

compounds. The compounds prepared by the classical ceramic method (solid state reaction) and calcinated at the temperature range from 1350 °C to 1500 °C were applied into the organic binder in mass tone and into the transparent ceramic glaze. The obtained results show that the colour coordinates were changed in the dependence on the calcination temperature and the method of preparation.

First, the preparation of ceramic pigments by the classical ceramic method and their subsequent application into the organic binder was studied (Tab. 2). The increasing calcination temperature resulted decrease in the value L^* (lightness) up to 1450 °C and pigments became darker. At temperature 1500 °C, there was a slight increase in the value of lightness. The growth of C value was more considerable at pigments synthesised at higher temperatures (1450, 1500 °C) and the increasing contribution of red colour (at 1450 °C; $a^* = 15.08$ and $C = 25.57$, resp. at 1500 °C; $a^* = -15.11$, $C = 24.90$, which has positive effect as well. All pigments provided blue-violet hue. This fact is confirmed from the values of $H°$, which lay in the range from 296° to 308°.

Tab. 2 *The colour properties and particle size distribution of $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ pigments prepared by classical ceramic method and applied into organic binder*

T [°C]	L*	a*	b*	C	H°	d$_{50}$ [µm]	span
1350	53.50	6.51	-13.07	14.60	296.48	7.24	5.22
1400	54.07	11.39	-17.92	21.23	302.44	8.71	6.43
1450	46.07	15.08	-20.87	25.57	305.85	9.02	5.25
1500	48.08	15.11	-19.79	24.90	307.36	12.75	4.89

From Tab. 3 is evident, that pigments which were prepared by dry mechanical activation provided worse results. The pigments prepared by using dry mechanical activation had rather a dark grey or dark blue-grey then violet colouration. It is caused by very low values of chroma C (especially at calcination temperature 1400 and 1450 °C) which resulted from low values of both colour coordinates. The increase of synthesis temperature had not a positive effect on colour properties. Thus, the best results were achieved at lowest calcination temperature 1350 °C. The negative changes of colouration were probably caused by the presence of secondary phase – cubic SnP_2O_7.

Tab. 3 *The colour properties and particle size distribution of $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ pigments prepared by dry mechanical activation and applied into organic binder*

T [°C]	L*	a*	b*	C	H°	ΔE$_{CIE}$*	d$_{50}$ [µm]	span
1350	52.83	7.67	-12.42	14.60	301.70	1.49	7.21	4.95
1400	54.72	1.58	-6.04	6.24	284.65	15.42	5.15	4.25
1450	53.82	2.59	-6.89	7.36	290.60	20.29	6.30	4.24

| 1500 | 58.54 | 6.71 | -11.46 | 13.28 | 300.35 | 15.79 | 6.33 | 4.04 |

The value of total colour difference ΔE_{CIE}^* was very low at 1350 °C. It means that colour difference between pigment which was prepared by classical ceramic method and pigment which were prepared by dry mechanical activation was imperceptible to the human eye. On the other hand, the highest value of total colour difference ΔE_{CIE}^* (20.29) was observed in the case of pigment synthesised at 1450 °C. This fact is mainly caused by the increase of lightness and decrease of both colour coordinates at pigment prepared by dry mechanical activation.

Tab. 4 The colour properties and particle size distribution of $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ pigments prepared by classical ceramic method and applied into ceramic glaze

T [°C]	L*	a*	b*	C	H°	d_{50} [µm]	span
1350	44.31	7.30	-22.91	24.04	287.90	7.24	5.22
1400	44.14	7.47	-23.38	24.54	287.72	8.71	6.43
1450	43.95	10.41	-23.47	25.67	293.90	9.02	5.25
1500	41.58	9.09	-24.95	26.55	290.02	12.75	4.89

The prepared pigments were applied into the ceramic glaze as well. The colouration of the samples in this application was different in the comparison with the application into the organic binder. The lightness L^* of pigments synthesised by the classical ceramic method was decreasing with the increasing temperature and is significantly lower than in the case of pigments prepared using dry mechanical activation. The share of red shade ($+a^*$) was growing with the increasing calcination temperature up to 1450 °C, where reached its maximum ($a^* = 10.41$). This trend is apparent also from the slightly increasing values of angle $H°$, which indicated a shift closer toward blue-violet colour.

Tab. 5 The colour properties and particle size distribution of $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ pigments prepared by dry mechanical activation and applied into ceramic glaze

T [°C]	L*	a*	b*	C	H°	ΔE_{CIE}^*	d_{50} [µm]	span
1350	45.80	7.59	-23.99	25.16	287.56	1.86	7.21	4.95
1400	51.39	6.95	-24.88	25.83	285.61	7.42	5.15	4.25
1450	51.24	6.91	-24.95	25.89	285.50	8.22	6.30	4.24
1500	48.97	7.98	-26.03	27.23	287.04	7.55	6.33	4.04

If we are talking about the application of the samples into the ceramic glaze, we can say, that in the comparison with the pigments prepared by classical ceramic method were obtained pigments whose colour was shifted closer toward to blue shades than blue-violet. At all pigments prepared by dry mechanical activation a

slight decrease of red shade in the final colour occurred in comparison with the previous method. The share of blue shade (-*b**) was growing with the increasing synthesis temperature. The colours of similar purity in comparison with ceramic method were acquired.

As in the application into the organic binder, the value of total colour difference was very low at 1350 °C (ΔE^*_{CIE} = 1.86) and the difference between samples was imperceptible to the human eye. The highest value of total colour difference ΔE_{CIE}^* (8.22) was observed in the case of pigment synthesised at 1450 °C. This fact is caused by significant increase of lightness *L** and slight decrease of value +*a**.

Particle size distribution

The calcination temperature and preparation method affect not only related colour properties but also particle size distribution. It belongs to the one of the most significant measured properties of synthesised powders and it can affect optical properties (final colour of pigments) and opacity. In the case of the classical ceramic method, the results showed that the growing synthesis temperature caused an increase of values d_{50}. These samples were characterised by higher mean values of d_{50}. Their values were in the range from approx. 7 to 13 µm. The lower values of mean particle size were obtained by dry mechanical activation. Their interval ranged from approx. 5 to 8 µm. From the values of *span* we can conclude, that the increasing calcination temperature caused a narrowing of the particle size distribution.

Conclusion

The aim of this research was to verify the different method of the preparation of the $Sn_{0.752}Co_{0.08}P_{0.16}Mn_{0.008}O_2$ pigment. The samples were synthesised by the classical ceramic method and by dry mechanical activation. In the order to find optimal calcination temperature, the starting mixtures were calcined in the temperature range from 1350 °C to 1500 °C.

The using classical ceramic method resulted in the obtaining of single-phased samples at all synthesis temperature. In the case of using dry mechanical activation, the presence of secondary minor phase – cubic SnP_2O_7 was observed in the temperature range from 1350 °C to 1400 °C. From presented results it can be concluded, that classical ceramic method provided better colour properties. The pigments which were prepared by using classical ceramic method were darker, they had the higher value of chroma *C* and higher values of hue angle *H°* in both applications. The best results gave pigment prepared by the classical using ceramic method at 1450 °C. At this sample the most significant increase in the contribution of red shade and the highest value of chroma *C* in both applications were achieved. Synthesised pigments doped by ions of manganese provided violet (classical ceramic method) and grey (dry mechanical activation) shades in the organic binder and blue-violet shades in the ceramic glaze. The mean of particle size d_{50} moved in range

approx. 6–13 µm in dependence on synthesis temperature and this particle size is appropriate for the potential using in ceramic glazes.

Acknowledgement

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